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Use of polymers containing vinylamine units as promoters for alkyldiketene sizing

- 5 The present invention relates to the use of polymers as promoters for the engine sizing of paper with alkyldiketenes.

Aqueous alkyldiketene dispersions which are stabilized with cationic starch or with anionic emulsifiers are commercial engine
10 sizes for paper. The full sizing effect of the papers sized with alkyldiketene dispersions is not developed until the sized papers are stored. Such papers therefore cannot further be processed, for example treated with coating slips, or printed on immediately after papermaking. Rather, they must be stored for at least 24
15 hours until a sufficient sizing effect has developed.

US-A-4,317,756 discloses a size mixture which contains a hydrophobic size reactive toward cellulose, such as an alkylketene dimer, and a cationic polymer, for example a
20 condensate of epichlorohydrin and bisaminopropylpiperazine. The cationic polymers increase the rate of development of the sizing, i.e. they act as promoters.

A more rapid development of the sizing effect of aqueous
25 alkyldiketene dispersions is achieved according to US-A-4,784,727 with the aid of terpolymers which contain styrene, N,N-dimethylaminoethyl (meth)acrylate and acrylonitrile as polymerized units.

30 WO-A-98/33979 discloses an aqueous dispersion of a reactive size for cellulose, which dispersion contains a cationic organic compound having a molar mass of less than 10 000 and an anionic stabilizer.

35 WO-A-00/23651 discloses aqueous, anionic size dispersions which are obtainable by dispersing a reactive size, such as an alkyldiketene or alkenylsuccinic anhydride, in water in the presence of an anionic dispersant. Dispersants used are, for example, condensates of naphthalenesulfonic acid and formaldehyde
40 or condensates of phenol, phenolsulfonic acid and formaldehyde or amphiphilic copolymers of hydrophobic monoethylenically unsaturated monomers and hydrophilic monomers having an anionic group. The dispersants may be present in the form of the free acids or of the alkali metal, alkaline earth metal and/or
45 ammonium salts. The size dispersions are added to the paper stock, it being possible, if required, concomitantly to use the drainage aids, flocculants and retention aids and fixing agents

usually employed in papermaking. Even with the use of anionic alkyldiketene dispersions, complete sizing of the paper does not occur immediately but, as in the case of the sizing of paper with alkyldiketene dispersions produced by cationic dispersing,
5 likewise only after relatively long storage of the sized paper.

EP-A-0 438 707 relates to a process for the production of paper, board and cardboard from a paper stock containing interfering substances, hydrolyzed homo- and copolymers of N-vinylformamide
10 having a degree of hydrolysis of at least 60% being used as fixing agents for interfering substances. These polymers are preferably used in combination with a cationic retention aid.

WO-A-97/05330 discloses the use of synthetic cationic polymers,
15 such as polyvinylamines and polyvinylamine hydrochlorides, as promoters for the engine sizing of paper with alkenylsuccinic anhydrides.

It is an object of the present invention to provide further
20 promoters for the engine sizing of paper with alkyldiketenes.

We have found that this object is achieved, according to the invention, by the use of polymers containing vinylamine units and having a K value (determined in 5% strength aqueous sodium
25 chloride solution at 25°C, a pH of 7 and a polymer concentration of 0.5% by weight) of from 30 to 150 as promoters for the engine sizing of paper with alkyldiketenes.

Suitable cellulose fibers for the production of paper, board and
30 cardboard are all types customary for this purpose, for example cellulose fibers from mechanical pulp and all fibers obtained from annual plants. Mechanical pulp includes, for example, groundwood, thermomechanical pulp (TMP), chemothermomechanical pulp (CTMP), pressure groundwood, semichemical pulp, high-yield
35 pulp and refiner mechanical pulp (RMP) and wastepaper. Chemical pulps are also suitable and may be used in bleached or in unbleached form. Examples of these are sulfate, sulfite and soda pulps. Unbleached pulps, which are also referred to as unbleached kraft pulp, are preferably used. Said fibers may be used alone or
40 as a mixture.

Suitable sizes for the preparation of the aqueous alkyldiketene dispersions are, for example, fatty alkyldiketenes which are obtainable from long-chain saturated or ethylenically unsaturated
45 acyl chlorides by elimination of hydrogen chloride with tertiary amines. The alkyldiketenes preferably contain 12 to 22 carbon atoms in the alkyl group. Suitable alkyldiketenes are, for

example, tetradecyldiketene, palmityldiketene, oleyldiketene, stearyldiketene and behenyldiketene. Alkyldiketenes having different alkyl groups, such as stearylpalmityldiketene, behenylstearyldiketene, behenyleleyldiketene or
5 palmitylbehenyldiketene, are also suitable. Stearyldiketene, palmityldiketene, behenyldiketene or a mixture of behenyldiketene and stearyldiketene is preferably used.

The fatty alkyldiketenes are processed to give aqueous
10 dispersions by first melting them and dispersing the melt under the action of shear forces, for example with the aid of an Ultraturrax apparatus, in water in the presence of cationic starch as stabilizer. Anionic compounds may also be used as a stabilizer. Processes for the preparation of anionic aqueous
15 dispersions of alkyldiketene are disclosed, for example, in WO-A-00/23651 (cf. pages 2 to 12). For the preparation of size dispersions, the alkyldiketenes are usually heated to above their melting point and are emulsified in molten form in water under the action of shear forces. For example, homogenizers are used
20 for this purpose. The dispersed sizes are stabilized in the aqueous phase using either a cationic starch or at least one anionic dispersant from the group consisting of the condensates of

- 25 (a) naphthalenesulfonic acid and formaldehyde,
(b) phenol, phenolsulfonic acid and formaldehyde,
(c) naphthalenesulfonic acid, formaldehyde and urea and
30 (d) phenol, phenolsulfonic acid, formaldehyde and urea.

The anionic dispersant may be present in the form of the free acids, of the alkali metal salts, of the alkaline earth metal
35 salts and/or of the ammonium salts. The ammonium salts may be derived either from ammonia or from a primary, secondary or tertiary amine, for example the ammonium salts of dimethylamine, trimethylamine, hexylamine, cyclohexylamine, dicyclohexylamine, ethanolamine, diethanolamine and triethanolamine being suitable.
40 The condensates described above are known and are commercially available. They are prepared by condensation of said components, it also being possible to use the corresponding alkali metal, alkaline earth metal or ammonium salts instead of the free acids. Suitable catalysts in the condensation are, for example, acids
45 such as sulfuric acid, p-toluenesulfonic acid and phosphoric acid. Naphthalenesulfonic acid or an alkali metal salt thereof is condensed with formaldehyde, preferably in a molar ratio of from

1 : 0.1 to 1 : 2, in general from 1 : 0.5 to 1 : 1. The molar ratio for the preparation of condensates of phenol, phenolsulfonic acid and formaldehyde is likewise in the abovementioned range, any desired mixtures of phenol and phenolsulfonic acid being used instead of naphthalenesulfonic acid in the condensation with formaldehyde. Instead of phenolsulfonic acid, it is also possible to use the alkali metal and ammonium salts of phenolsulfonic acid. The condensation of the abovementioned starting materials can, if required, additionally be carried out in the presence of urea. For example, from 0.1 to 5 mol of urea are used per mol of naphthalenesulfonic acid or per mol of the mixture of phenol and phenolsulfonic acid.

The condensates have, for example, molar masses of from 800 to 100 000, preferably from 1 000 to 30 000, in particular from 4 000 to 25 000. Preferably used anionic dispersants are salts which are obtained, for example, by neutralizing condensates with lithium hydroxide, sodium hydroxide, potassium hydroxide or ammonia. The pH of the salts is, for example, from 7 to 10.

Other suitable anionic dispersants are amphiphilic copolymers of

- (i) hydrophobic monoethylenically unsaturated monomers and
- (ii) hydrophilic monomers having an anionic group, such as monoethylenically unsaturated carboxylic acids, monoethylenically unsaturated sulfonic acids, monoethylenically unsaturated phosphonic acids or mixtures thereof.

Suitable hydrophobic monoethylenically unsaturated monomers

- (a) are, for example, olefins of 2 to 150 carbon atoms, styrene α -methylstyrene, ethylstyrene, 4-methylstyrene, acrylonitrile, methacrylonitrile, esters of monoethylenically unsaturated C_3 - to C_5 -carboxylic acids and monohydric alcohols, amides of acrylic acid or methacrylic acid with C_1 - to C_{24} -alkylamines, vinyl esters of saturated monocarboxylic acids of 2 to 24 carbon atoms, diesters of maleic acid or fumaric acid with monohydric C_1 - to C_{24} -alcohols, vinyl ethers of alcohols of 3 to 24 carbon atoms or mixtures of said compounds.

The amphiphilic copolymers contain, as hydrophilic monomers (b), for example, monoethylenically unsaturated C_3 - to C_{10} -carboxylic acids or anhydrides thereof, 2-acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, styrenesulfonic acid, vinylphosphonic

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acid, salts of said monomers or mixtures thereof as hydrophilic monomers having an anionic group

in the form of polymerized units. Particularly preferred are
 5 aqueous size dispersions which contain, as an anionic dispersant, amphiphilic copolymers of

(a) α -olefins of 4 to 12 carbon atoms, styrene or mixtures thereof as hydrophobic monomers and

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(b) maleic acid, acrylic acid, methacrylic acid, monoesters of maleic acid and alcohols of 1 to 25 carbon atoms or alkoxylation products of such alcohols, monoamides of maleic acid, salts of said monomers or mixtures of these compounds
 15 as hydrophilic monomers having an anionic group

in the form of polymerized units and have a molar mass M_w of from 1 500 to 100 000.

20 Preferred anionic dispersants are copolymers of maleic anhydride with C_4 - to C_{12} -olefins, particularly preferably C_8 -olefins, such as 1-octene and diisobutene. Diisobutene is very particularly preferred. The molar ratio of maleic anhydride to olefin is, for example, from 0.9 : 1 to 3 : 1, preferably from 0.95 : 1 to 1.5 :

25 1. These copolymers are preferably used in hydrolyzed form as aqueous solutions or dispersions, the anhydride group being present in opened form and preferably some or all of the carboxyl groups having been neutralized. The following bases are used for the neutralization: alkali metal bases, such as sodium hydroxide,
 30 potassium hydroxide, sodium carbonate or potassium carbonate, alkaline earth metal salts, such as calcium hydroxide, calcium carbonate or magnesium hydroxide, ammonia, primary, secondary or tertiary amines, such as triethylamine, triethanolamine, diethanolamine, ethanolamine, morpholine, etc.

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If the amphiphilic copolymers in the form of the free acids are not sufficiently water-soluble, they are used in the form of water-soluble salts, for example the corresponding alkali metal, alkaline earth metal and ammonium salts being used. The molar

40 mass M_w of the amphiphilic copolymers is, for example, from 800 to 250 000, in general from 1 000 to 100 000, preferably from 3 000 to 20 000, in particular from 1 500 to 10 000. The acid numbers of the amphiphilic copolymers are, for example, from 50 to 500, preferably from 150 to 300, mg KOH/g of polymer.

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The amphiphilic copolymers are used, for example, in amounts of from 0.05 to 20, preferably from 0.5 to 10, % by weight, based on the reactive size, as an anionic dispersant for the preparation of the size dispersions. The amphiphilic copolymers are

5 preferably used in amounts of from 0.1 to 2, in particular from 0.6 to 1, % by weight, based on the size to be dispersed. When amphiphilic copolymers are used alone as dispersants, the aqueous size dispersions which are formaldehyde-free and have a long shelf life are obtained.

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To prepare aqueous, anionic size dispersions, for example, an aqueous solution of at least one condensate or of at least one amphiphilic copolymer can be initially taken and the size dispersed therein at, for example, from 20 to 100°C, preferably
15 from 40 to 90°C. The size is preferably added in the form of a melt and is dispersed with vigorous stirring or shearing. The resulting dispersion is cooled in each case. For example, aqueous, anionic size dispersions which contain from 6 to 65% by weight of a dispersed alkyl diketene as a size can be prepared in
20 this manner. Highly concentrated sized dispersions which contain, for example, from 25 to 60% by weight of an alkyl diketene as a size in the presence of from 0.1 to 5.0% by weight of a condensate of naphthalenesulfonic acid and formaldehyde of at least one condensate (b), (c) and/or (d) in dispersed form are
25 preferred.

Further preferred size dispersions contain from 25 to 60% by weight of an alkyl diketene as a size and from 0.1 to 5.0% by weight of an amphiphilic copolymer of

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(i) from 95 to 50% by weight of isobutene, diisobutene, styrene or a mixture thereof and

(ii) from 5 to 50% by weight of acrylic acid, methacrylic acid,
35 maleic acid, a monoester of maleic acid or a mixture thereof

or of a water-soluble salt of such a copolymer.

Such highly concentrated size dispersions have a relatively low
40 viscosity, for example from 20 to 100 mPa.s (measured using a Brookfield viscometer and at 20°C). In the preparation of the aqueous dispersions, the pH is, for example, from 2 to 8, preferably from 3 to 4. Aqueous anionic size dispersions having a mean particle size of the size of from 0.1 to 3, preferably from
45 0.5 to 1.5, μm are obtained.

The anionic alkyldiketene dispersions can, if required, be rendered cationic by adding a sufficient amount of cationic starch.

- 5 According to the invention, at least one polymer containing vinylamine units is used as a promoter for alkyldiketene size. The amount of cationic polymers is, for example, from 0.01 to 2.0, preferably from 0.01 to 0.1, % by weight, based on dry cellulose fibers.

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Polymers containing vinylamine units are known, cf.

US-A-4,421,602, US-A-5,334,287, EP-A-0 216 387, US-A-5,981,689, WO-A-00/63295 and US-A-6,121,409. They are prepared by hydrolysis of open-chain polymers containing N-vinylcarboxamide units. These

- 15 polymers are obtainable, for example, by polymerization of N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide and N-vinylpropionamide. Said monomers can be polymerized either alone or together with other monomers.

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Suitable monoethylenically unsaturated monomers which are copolymerized with the N-vinylcarboxamides are all compounds copolymerizable therewith. Examples of these are vinyl esters of saturated carboxylic acids of 1 to 6 carbon atoms, such as vinyl

- 25 formate, vinyl acetate, vinyl propionate and vinyl butyrate, and vinyl ethers, such as C₁- to C₆-alkyl vinyl ethers, e.g. methyl or ethyl vinyl ether. Further suitable comonomers are esters, amides and nitriles of ethylenically unsaturated C₃- to C₆-carboxylic acids, for example methyl acrylate, methyl methacrylate, ethyl
- 30 acrylate and ethyl methacrylate, acrylamide and methacrylamide and acrylonitrile and methacrylonitrile.

Further suitable carboxylic esters are derived from glycols or polyalkylene glycols, in each case only one OH group being

- 35 esterified, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate and acrylic monoesters of polyalkylene glycols having a molar mass of from 500 to 10 000. Further suitable comonomers are esters of
- 40 ethylenically unsaturated carboxylic acids with amino alcohols, for example dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl
- 45 acrylate and diethylaminobutyl acrylate. The basic acrylates can be used in the form of the free bases, of the salts with mineral acids, such as hydrochloric acid, sulfuric acid or nitric acid,

of the salts with organic acids, such as formic acid, acetic acid or propionic acid, or of the sulfonic acids or in quaternized form. Suitable quaternizing agents are, for example, dimethyl sulfate, diethyl sulfate, methyl chloride, ethyl chloride and 5 benzyl chloride.

Further suitable comonomers are amides of ethylenically unsaturated carboxylic acids, such as acrylamide, methacrylamide and N-alkylmono- and diamides of monoethylenically unsaturated 10 carboxylic acids having alkyl radicals of 1 to 6 carbon atoms, e.g. N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-propylacrylamide and tert-butylacrylamide, and basic (meth)acrylamides, e.g. dimethylaminoethylacrylamide, dimethylaminoethylmethacrylamide, 15 diethylaminoethylacrylamide, diethylaminoethylmethacrylamide, dimethylaminopropylacrylamide, diethylaminopropylacrylamide, dimethylaminopropylmethacrylamide and diethylaminopropylmethacrylamide.

20 Other suitable comonomers are N-vinylpyrrolidone, N-vinylcaprolactam, acrylonitrile, methacrylonitrile, N-vinylimidazole and substituted N-vinylimidazoles, e.g. N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole, N-vinyl-5-methylimidazole and N-vinyl-2-ethylimidazole and 25 N-vinylimidazolines, such as N-vinylimidazoline, N-vinyl-2-methylimidazoline and N-vinyl-2-ethylimidazoline. N-Vinylimidazoles and N-vinylimidazolines are used not only in the form of the free bases but also in a form neutralized with mineral acids or organic acids or in quaternized form, the 30 quaternization being carried out preferably with dimethyl sulfate, diethyl sulfate, methyl chloride or benzyl chloride. Diallyldialkylammonium halides, e.g. diallyldimethylammonium chloride, are also suitable.

35 The copolymers contain, for example,

- from 95 to 5, preferably from 90 to 10, mol% of at least one N-vinylcarboxamide and
- 40 - from 5 to 95, preferably from 10 to 90, mol% of other monoethylenically unsaturated monomers copolymerizable therewith

in the form of polymerized units. The comonomers are preferably 45 free of acid groups.

Polymers containing vinylamine units are preferably prepared starting from homopolymers of N-vinylformamide or from copolymers which are obtainable by copolymerization of

5 - N-vinylformamide with

- vinyl formate, vinyl acetate, vinyl propionate, acrylonitrile, N-vinylcaprolactam, N-vinylurea, N-vinylpyrrolidone or C₁- to C₆-alkyl vinyl ethers

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and subsequent hydrolysis of the homopolymers or of the copolymers with formation of vinylamine units from the polymerized N-vinylformamide units, the degree of hydrolysis being, for example, from 1 to 100, preferably from 70 to 100,

15 mol%. The degree of hydrolysis is in particular from 80 to 100 mol%. The hydrolysis of the polymers described above is effected by the action of acids, bases or enzymes by known processes. With the use of acids as a hydrolyzing agent, the vinylamine units of the polymers are present as the ammonium
20 salt, whereas the free amino groups form in the hydrolysis with bases. The polymers containing vinylamine units can be used in the form of the free bases or of the ammonium salts or in quaternized form as promoters.

25 In most cases, the degree of hydrolysis of the homopolymers and copolymers used is from 90 to 95 mol%. The degree of hydrolysis of the homopolymer is equivalent to the content of vinylamine units in the polymers. In the case of copolymers which contain vinyl esters as polymerized units, hydrolysis of the ester groups
30 with formation of vinyl alcohol units may occur in addition to the hydrolysis of the N-vinylformamide units. This is the case in particular when the hydrolysis of the copolymers is carried out in the presence of sodium hydroxide solution. Acrylonitrile present in the form of polymerized units is likewise chemically
35 modified in the hydrolysis. For example, amido groups or carboxyl groups form here. The homo- and copolymers containing vinylamine units can, if required, contain up to 20 mol% of amidine units, which form, for example, by reaction of formic acid with two
40 amino group with a neighboring amido group, for example of N-vinylformamide present in the form of polymerized units. The molar masses M_w of the polymers containing vinylamine units are, for example, from 500 to 10 million, preferably from 1 000 to 5 000 000 (determined by light scattering). This molar mass range
45 corresponds, for example, to K values of from 30 to 150, preferably from 60 to 90 (determined according to H. Fikentscher in 5% strength aqueous sodium chloride solution at 25°C, a pH of 7

and a polymer concentration of 0.5% by weight). Cationic polymers which have K values of from 85 to 90 are particularly preferably used.

- 5 The average molar masses M_w of the polymers containing vinylamine units are, for example, from 8 000 to 2 million, preferably from 70 000 to 240 000.

The polymers containing vinylamine units are preferably used in
10 salt-free form. Salt-free aqueous solutions of polymers containing vinylamine units can be prepared, for example, from the salt-containing polymer solutions described above with the aid of ultrafiltration over suitable membranes with cut-off of, for example, 1 000 to 500 000, preferably from 10 000 to 300 000,
15 Dalton.

Derivatives of polymers containing vinylamine units may also be used as cationic polymers. For example, it is possible to prepare a large number of suitable derivatives from the polymers
20 containing vinylamine units by amidation, alkylation, sulfonamide formation, urea formation, thiourea formation, carbamate formation, acylation, carboxymethylation, phosphonomethylation or Michael addition of the amino groups of the polymer. Of particular interest here are uncrosslinked polyvinylguanidines,
25 which are obtainable by reaction of polymers containing vinylamine units, preferably polyvinylamines, with cyanamide (R^1R^2N-CN , where R^1 and R^2 are H, C_1 - to C_4 -alkyl, C_3 - to C_6 -cycloalkyl, phenyl, benzyl, alkyl-substituted phenyl or naphthyl), cf. US-A-6,087,448, column 3, line 64 to column 5,
30 line 14.

The polymers containing vinylamine units also include hydrolyzed graft polymers of, for example, N-vinylformamide on polyalkylene glycols, polyvinyl acetate, polyvinyl alcohol,
35 polyvinylformamides, polysaccharides, such as starch, oligosaccharides or monosaccharides. The graft polymers are obtainable by subjecting, for example, N-vinylformamide to free radical polymerization in an aqueous medium in the presence of at least one of said grafting bases, if required together with other
40 copolymerizable monomers, and then hydrolyzing the grafted-on vinylformamide units in a known manner to give vinylamine units.

Preferred polymers containing vinylamine units are vinylamine homopolymers, from 10 to 95% hydrolyzed polyvinylformamides,
45 partially or completely, preferably 90 - 95%, hydrolyzed copolymers of vinylformamide and vinyl acetate, vinyl alcohol,

vinylpyrrolidone or acrylamide, in each case having K values of from 30 to 150, in particular from 60 to 90.

Paper, board and cardboard are usually produced by draining with
 5 suspension of cellulose fibers. The use of kraft pulp is particularly preferred. Also of particular interest is the use of TMP and CTMP. The pH of the cellulose fiber suspension is, for example, from 4 to 8, preferably from 6 to 8. The paper stock can be drained batchwise or continuously on a paper machine. The
 10 sequence of addition of cationic polymer, engine size and retention aid can be freely chosen. However, a procedure in which a mixture of an aqueous alkyl diketene dispersion and at least one compound containing vinylamine units, or first the cationic polymer, preferably polyvinylamine, and then at least one
 15 alkyl ketene dimer, or a mixture of alkyl ketene dimers, are added to the aqueous cellulose fiber suspension is preferred. Thereafter, preferably at least one retention aid is metered. According to another embodiment of the invention, first at least one alkyl diketene, then the retention aid and finally the polymer
 20 containing vinylamine units is metered. Alkyl ketene dimers are used, for example, in amounts of from 0.01 to 2, preferably from 0.01 to 0.2, % by weight, based in each case on dry paper stock, in the engine sizing of paper. If the aqueous dispersion of the alkyl ketene dimers already contains at least one polymer
 25 containing vinylamine units and to be used as a promoter, for example, from 0.0001 to 2, preferably from 0.001 to 1, % by weight, based on alkyl ketene dimer, of the promoter are used.

After the paper stock has been drained and the paper product
 30 dried, engine-sized paper products, such as paper, board or cardboard having a basis weight of, for example, from 20 to 400, preferably from 40 to 220, g/m² are obtained.

The paper stock is preferably drained additionally in the
 35 presence of a retention aid. Apart from anionic retention aids or nonionic retention aids, such as polyacrylamides, cationic polymers are preferably used as retention aids and as drainage aids. A significant improvement in the runability of the paper machine is thus achieved.

40 Cationic retention aids which may be used are all products commercially available for this purpose. These are, for example, cationic polyacrylamides, polydiallyldimethylammonium chlorides, high molecular weight polyvinylamines, high molecular weight
 45 polyvinylamines having K values of more than 150, polyethyleneimines, polyamines having a molar mass of more than 50 000, modified polyamines which are grafted with ethyleneimine

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and are uncrosslinked or crosslinked, polyetheramides, polyvinylimidazoles, polyvinylpyrrolidines, polyvinylimidazolines, polyvinyltetrahydropyrines, poly(dialkylaminoalkyl vinyl ethers), poly(dialkylaminoalkyl

- 5 (meth)acrylates) in protonated or in quaternized form and polyamidoamines obtained from a dicarboxylic acid, such as adipic acid, and polyalkylenepolyamines, such as diethylenetriamine, which are grafted with ethyleneimine and crosslinked with polyethylene glycol dichlorohydrin ethers according to
- 10 DE-B-24 34 816, or polyamidoamines which have been reacted with epichlorohydrin to give water-insoluble condensates, and copolymers of acrylamide or methacrylamide and dialkylaminoethyl acrylates or methacrylates, for example copolymers of acrylamide and dimethylaminoethyl acrylate in the form of the salt with
- 15 hydrochloric acid or in a form quaternized with methyl chloride. Further suitable retention aids are microparticle systems comprising cationic polymers, such as cationic starch, and finely divided silica or comprising cationic polymers, such as cationic polyacrylamide, and bentonite.

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The cationic polymers which are used as retention aids have, for example, Fikentscher K values of more than 150 (determined in 5% strength aqueous sodium chloride solution at a polymer concentration of 0.5% by weight, a temperature of 25°C and a pH of

25 7). They are preferably used in amounts of from 0.01 to 0.3% by weight, based on dry cellulose fibers.

In the examples which follow, percentages are by weight, unless evident otherwise from the context. The K values were determined

30 according to H. Fikentscher, Cellulose-Chemie, 13 (1932), 58-64 and 71-74, in 5% strength aqueous sodium chloride solution at 25°C and a pH of 7 at a polymer concentration of 0.5% by weight. The molar masses M_w of the polymers were determined by light scattering.

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Examples

Cobb value

- 40 The determination was carried out according to DIN 53 132 by storing the paper sheets in water for a period of 60 seconds. The water absorption is stated in g/m².

The HST values were determined with the aid of the Hercules Size

45 Tester according to TAPPI Test Method T530 pm-89.

Dispersion 1

Aqueous dispersion having a solids content of 12% of stearyldiketene and 2% of cationic starch.

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Dispersion 2

Aqueous dispersion having a solids content of 12% of stearyldiketene and 2% of cationic starch and additionally 0.12%,
10 based on stearyldiketene, of a polyvinylamine having a K value of 90.

Dispersion 3

15 Aqueous dispersion having a solids content of 12% of stearyldiketene and 2% of cationic starch and additionally 0.12%, based on stearyldiketene, of a hydrolyzed polyvinylformamide having a degree of hydrolysis of 81% and a K value of 90.

20 Dispersion 4

Aqueous dispersion having a solids content of 12% of stearyldiketene and 2% of cationic starch and additionally 0.12%, based on stearyldiketene, of a modified, hydrolyzed
25 polyvinylformamide having a degree of hydrolysis of 95% and a K value of 90, the modification having been carried out by reacting the partly hydrolyzed polyvinylformamide (67 mol% of vinylformamide units and 33 mol% of vinylamine units) according to example 2 of WO-A-00/26468.

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Example 1

Those amounts of dispersions 1 to 4 which are stated in tables 1 and 2, 20% of calcium carbonate, 0.6% of a cationic cornstarch
35 and 0.04% of a cationic polyacrylamide (Polymin® KE2020) as a retention aid, based in each case on dry cellulose fiber mixture, were added to a paper stock having a consistency of 8 g/l and comprising a completely bleached mixture of 70% of pine sulfate pulp and 30% of birch sulfate pulp having a freeness of 35°
40 (Schopper-Riegler). The pH of the mixture was brought to 7.0. The mixture was then processed on a Rapid-Köthen sheet former to give a sheet having a basis weight of 100 g/m². The sheet was then dried on a steam-heated drying cylinder at 90°C to a water content of 7%. Immediately after the drying, the Cobb value and the HST
45 value of the sheets were determined. The sheets were then stored for 24 hours at 25°C and a relative humidity of 50%. The

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measurements were then repeated. The results obtained are shown in tables 1 and 2.

Table 1

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Test No.	Dispersion	[%] stearyldiketene, based on dry paper stock	Cobb 60 in g/m ² immediately	Cobb 60 in g/m ² after 24 h
1	Dispersion 1	0.07	56	32
2	Dispersion 1	0.1	45	25
3	Dispersion 2	0.07	44	29
4	Dispersion 2	0.1	33	25
5	Dispersion 3	0.07	40	28
6	Dispersion 3	0.1	34	24
7	Dispersion 4	0.1	31	24

Tests no. 1 and 2 are comparative examples and tests 3 to 7 are examples according to the invention.

20 Table 2

Test No.	Dispersion	Amount of dispersion % fiber mass	HST in sec. immediately	HST in sec. after 24 h
8	Dispersion 1	0.07	32	122
9	Dispersion 1	0.1	128	256
10	Dispersion 2	0.07	92	143
11	Dispersion 2	0.1	187	299
12	Dispersion 3	0.07	88	151
13	Dispersion 3	0.1	167	278
14	Dispersion 4	0.1	195	295

Tests no. 8 and 9 are comparative examples and tests 10 to 14 are examples according to the invention.

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